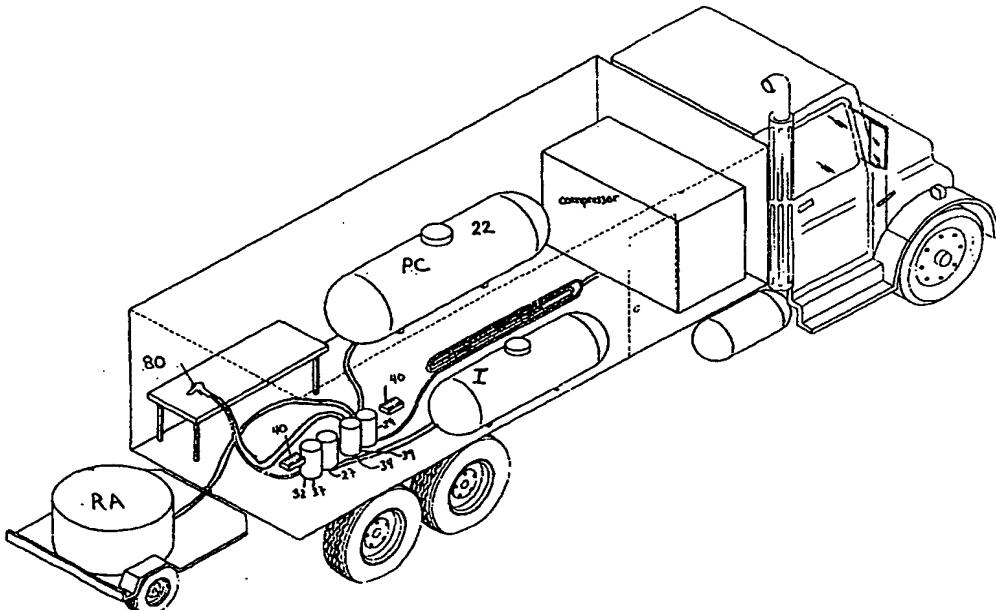




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(54) Title: BITUMINOUS POLYURETHANE INTERPENETRATING ELASTOMERIC NETWORK COMPOSITIONS			
(57) Abstract			
<p>The elastomeric polyurethane interpenetrating network compositions of the invention are developed by <i>in situ</i> reaction of polyols with different isocyanates and polyisocyanates in bituminous material. Suitable bituminous materials include asphalt, coal tar, polymer modified asphalt, oxidized, and unoxidized asphalt. The composition is preferably formed at a temperature between 200 °F and 350 °F. The reaction kinetics can be accelerated by including catalysts and curing agents. The reaction kinetics were followed by measuring the torque increase as a function of reaction time. The gelation time is measured at the maximum torque. For testing, the bituminous polyurethane interpenetrating network elastomeric compositions were hot-sprayed-applied (200 °F-350 °F) on different substrates such as concrete, metal, wood, built-up roofing systems, polyurethane foams, and other construction materials with a specially designed spray applicator system. The coated substrates were evaluated for their physical and mechanical properties, adhesion, static and dynamic puncture resistance, wind-up lift test, and other properties. Bituminous polyurethane interpenetrating network elastomer compositions of the invention are resistant to solvents, oil and acid. Bituminous polyurethane interpenetrating network elastomers are suitable for a wide variety of applications including but not limited to roofing, new construction, and wall and foundation waterproofing applications.</p>			



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BITUMINOUS POLYURETHANE
INTERPENETRATING ELASTOMERIC NETWORK COMPOSITIONS

TECHNICAL FIELD

5 This invention relates to the *in situ* generation and incorporation of polyurethane prepolymers generated within a matrix of bituminous material such as asphalt. The resulting bituminous polyurethane interpenetrating elastomeric network compositions can be applied as coatings and sealants for roofing, coverings, and
10 construction waterproofing applications, as well as other applications.

BACKGROUND ART

15 Polyurethanes are extensively used as coatings and sealants in housing, construction, furniture, and other industries. Polyurethane prepolymers are generally developed by reacting different polyols with di- or poly- isocyanates in varying ratios. Figure 2 depicts a reaction between a polyol and diisocyanate. Without more, polyurethanes are hard, water-resistant, slippery
20 when wet, and tend to degenerate when exposed to ultra-violet light.

25 "Bituminous material" is meant to include bitumen, asphalt, coal tar, and performance-rated asphalt. Due to the low cost of bituminous material, its relatively high penetration value when applied to most porous surfaces, weather-resistant nature, and impermeability to water, bituminous material has traditionally been used as a main component of protective films, adhesive binders in
30 asphalt emulsions (M. Lalanne and J. Serfass, U.S. Patent No. 4,724,245), in blends used for paving and roofing, joint sealants, paints, and other end uses. Existing unreinforced bituminous materials tend to crack during normal seasonal thermal expansion. In addition, typical bituminous materials are difficult to apply and take a long time (days) to cure completely.

35 Attempts to provide a blend of a liquid, preferably an ambient-curable prepolymer, with bituminous material have been made (H. Lucke, U.S. Patent No. 4,871,792). In the past, several methods were developed to increase the compatibility between the bituminous binder and polyurethanes, either by using a modified

clay (R.J. Janoski, U.S. Patents Nos. 5,421,876 and 5,319,008), or pre-treating the bituminous materials before mixing with polyurethane prepolymer (M. Shihadeh, U.S. Patent No. 3,980,597).

Several attempts to develop a rubberized bituminous material using crumb rubber have also been made. Methods are available, reported, and in practice today. Crumb rubber from recycled car and truck tires improves wear resistance (D.W. Causyn and K. Thys, PCT Int. Appl. WO 9221820), lowers temperature fracture properties (G.R. Morrison and S.A.M. Hesp., J. Mater. Sci. 30(10), 2584 (1995) and A. Coomaraswamy, S. Manolis and S. Hesp., Am. Chem. Soc. Div. Fuel. Chem., 41(4), 1322 (1996)); and enhances coating performance and safety of the coated surface (M. Wm. Rouse, Rubber World, 212(2), 23 (1995)). Most of these applications are used in the paving industry, anti-skid mats for playgrounds, and running tracks (H.L. Draper, D.F. Levy, and D.W. Gagle, U.S. Patent No. 3,547,674).

Apart from the use of crumb rubber, other polymers are used to modify asphalt (M.E. Labib, G.M. Memon, and B.H. Chollar, Prepr. Pap. - Am. Chem. Soc., Div. Fuel. Chem., 41(4), 1209 (1996), I.K. Negulescu and W.H. Daly, Annu. Tech. Conf., Soc. Plat. Eng. 54th (vol. 1), 1175 (1996). The thermoplastic nature of these existing polymer modified bituminous materials limits their coating and sealant applications.

These past attempts to incorporate a resin within a bituminous material have failed for a combination of reasons. First, polyurethanes and bituminous materials are not miscible because polyurethanes are polar, while bituminous materials are non-polar. Second, without more, the reaction rate between the reagents forming the polyurethane (polyol and isocyanate) is slow enough that the reagents separate from the bituminous material, polymerize, and form non-integrated, heterogenous products. These heterogenous products do not produce synergistic qualities such as increased strength and ease of application.

35

DISCLOSURE OF INVENTION

Owing to the advantages of polymer modified bituminous materials, this invention is a further novel modification of bituminous materials with polyurethanes, by *in situ* generation of

their prepolymers, so that the prepared bituminous polyurethane interpenetrating elastomeric network compositions will be stronger, easier to apply, and less expensive than the conventional mixing of polyurethane prepolymers with bituminous material. The mixing 5 of polyurethane prepolymer with the rubberized bituminous material at the molecular level results from improved miscibility. In turn, improved miscibility improves the physical and mechanical properties of the coatings and sealants.

According to the method of the invention, the polyol and 10 bituminous materials are mixed separately from the isocyanate. The polyol and molten bituminous material are more miscible than prepolymerized polyurethane and bituminous material. Next, a catalyst and curing agent can be added to either of the polyol or isocyanate. The polyol/bituminous material mixture is then mixed 15 thoroughly with the isocyanate immediately before application. The catalyst causes the polyurethane to form rapidly (in as little as seconds) within the bituminous material to form an effectively-homogenous, three-dimensional matrix.

The properties of the resulting matrix can be controlled by 20 changing the formulation. By increasing the proportion of cross-linking agents such as diisocyanate, the strength of the product is increased. By reducing the proportions of cross-linking agents, the flexibility of the materials can be increased. Increased strength is useful in applications such as building reinforcement. 25 Increased flexibility is useful in applications such as coating a running track or manufacturing o-rings.

A curing agent can be added to decrease the time before a permanent matrix is formed. Curing agent can reduce the gelation 30 time to as little as seconds. Reduced gelation time is useful to expedite the completion of jobs such as filling cracks and crevices. A curing agent can be omitted or limited in situations requiring a longer time before setting. A longer setting time can be desirable when the material is used as an adhesive and time is required to position the materials being adhered.

35 These materials were tested as coatings, sealants, and adhesives on a range of substrates. These materials can be generated at the job site, and are applied to various surfaces,

through our uniquely designed pumping, metering, mixing, and spraying system.

The present invention achieves the additional advantages set forth below by providing a unique method of modifying polyurethanes into useful compositions which meet the essential requirements for coatings and sealants. The asphalt/bitumen components provide processability of the resultant coatings and sealants. The rubber component provides frictional and abrasion resistance as well as ultra-violet radiation resistance to the coatings and sealants.

5 The unique method of producing these polymers yields easy applications as well as an overall decrease in the coating cost.

10 The bituminous polyurethane interpenetrating elastomeric network compositions produced have improved adhesion. The highly reactive urethane prepolymer gives better adhesion to different substrates.

15 The instant invention will now be described with particular reference to the accompanying drawing.

BRIEF DESCRIPTION OF DRAWINGS

20 Figure 1 is a schematic representation of the process of the instant invention.

Figure 2 is a prior-art chemical reaction depicting the formation of a typical polyurethane prepolymer from a polyol and diisocyanate.

25 Figure 3 is a table summarizing a series of controlled experiments containing different formulations.

Figure 4 is a table summarizing a series of controlled experiments utilizing different curing agents.

30 Figure 5 is a table summarizing a series of controlled experiments utilizing different bituminous materials.

Figure 6 is a perspective view of a mobile apparatus for the preparation of a bituminous polyurethane interpenetrating elastomeric network composition.

35 Figure 7 is a table listing a most preferred embodiment of the composition at the time of filing.

BEST MODE FOR CARRYING OUT THE INVENTION

Polyurethanes are widely used as coatings as well as sealant compounds because they adhere to a variety of substrates, resist scratching, and resist moisture. However, their uses are limited due to the high cost associated with application, degradation caused by ultra-violet light exposure, and slipperiness. The several compositions developed in the present invention are useful for converting polyurethanes into coatings as well as sealant compositions by a melt blending process. The first step includes the premixing of polyol(s) with the bituminous material already at its molten temperature to form a reagent mixture. The reagent mixture is carried separately from the isocyanate to the mixing head by heated hoses. At the mixing head, the reagent mixture and isocyanate are mixed. The polyurethane prepolymer forms as the reagent material and isocyanate mix. These materials are metered through a narrow metallic tube for sufficient molecular weight buildup and sprayed under pressure through a suitable spray apparatus.

Applications of the invention include the use of:

- bituminous materials such as asphalt, polymer and rubber enriched performance grade asphalt, and coal tar;
- new and recycled crumb rubber and synthetic rubber;
- polyols such as PPG, PEG, POTMG, HTPD, castor oil, and vegetable oils of different molecular weight and functionality; and
- isocyanates such as polymeric MDI as well as other dimeric and polymeric isocyanates.

In each of the following examples, the products were prepared in a common related manner. The bituminous material was prepared by degrading and dissolving crumb tire rubber in hot mix asphalt and heated to at least the molten temperature of the asphalt. The crumb rubber content in the asphalt component was between zero and seventy-five percent (0 - 75%) by weight. The rubberized asphalt was preheated between 125°C and 225°C in a separate vessel and this mixture is called component A. The polyol, either single or in combination of more than one, was catalyzed preferably with dibutyltin dilaurate (1-5% of the polyol weight) with constant

stirring in a separate vessel and is called component B. The isocyanate (dimeric and polymeric either alone or in combination) was placed in another separate vessel and is called component C. All three components were metered at varying compositions, mixed 5 immediately before spraying, and the resultant composition sprayed onto different substrates. The substrate may be any type of concrete, wood, metal, rubber, asphalt, or other commonly used roofing material.

10

EXAMPLE 1

Components B and C were mixed to form the polyurethane prepolymer, and the resultant composition was then mixed with component A *in situ* and then sprayed on a pre-fabricated aluminum dye at different thicknesses (e.g. 2mm, 4mm, 6mm, etc.). The 15 resulting bituminous polyurethane interpenetrating elastomeric network composition was then allowed to cure for twenty-four hours at 25°C and post-cured for five days at 25°C. All the samples were die cut for different test specimens. The viscosity, stress-strain properties, and other physical and mechanical properties should be 20 tested in accordance with procedures set forth in ASTM D 412.

EXAMPLE 2

By the same procedure, rubberized asphalt made from rubber sources, was used including virgin rubbers (styrene-butadiene 25 rubbers, butadiene rubbers, butyl rubbers, EPDM rubber, natural rubber, rubber made from other block copolymers and polymers of similar nature) and waste rubbers from other resources including off-specification rubbers and off-specification compounds from compounding operations.

30

EXAMPLE 3

By the same procedure as Example 1, the component B was substituted with other polyols, polyester polyols of different types and different molecular weight, polyether polyols of 35 different types and different molecular weights, polyol substitutes from vegetable oils such as caster oils and oils of similar nature. These components were either used alone or in combination with each other.

EXAMPLE 4

By the same procedure as Example 1, the component C was substituted with other di and/or polyisocyanates.

5

EXAMPLE 5

By the same procedure as Example 1, the catalyst was substituted with others.

10 By the same procedure as Example 1, the different ratios of components B with components C are tested.

EXAMPLE 7

15 By the same procedure as Example 1, the reactions were tested at different temperatures.

EXAMPLE 8

By the same procedure as Example 1, the reactions were carried out in different residence time (reaction time) and the materials tested for their physical and mechanical properties.

20

EXAMPLE 9

By the same procedure as Example 1, the coating is applied in sequence to study the colorability, and compatibility is tested.

25

EXAMPLE 10

Several selected formulations were sprayed on several substrates, including wood, metals, concrete, bricks, rubbers, asphalt binders, and substrates of similar nature. The adhesion between these coatings and these substrates is measured by 30 measuring the peel strength.

A series of controlled experiments were conducted to determine the effect of varying the formulation of the composition. The results of these experiments are listed in Figures 3, 4, and 5. In these experiments, unless specifically stated, the following methods were used. First, a required amount of asphalt was placed in a one quart (1 qt) tin container. The container was placed in an electric heating mantel. The desired temperature was maintained

using a controller having an accuracy of plus or minus three degrees Fahrenheit (+/- 3° F). The temperature of the liquid contents in the container was monitored by a sensor immersed in the liquid asphalt mixture. The mixture was mixed using a stirrer. 5 The stirrer utilized an overhead motor with a digital display of speed and torque. Torque was used to measure the viscosity of the mixture. The torque was monitored throughout the duration of the reaction. In the experiments, the polyol was preheated. If any curing agent or catalyst was included, they were added to the 10 polyol. The polyol was then added to the asphalt and mixed for twenty minutes (20 min). The isocyanate was added gradually (1-3) seconds to the mixture. The gelation point was determined from the plot of time versus torque. Each experiment was repeated to verify the reproducability and accuracy of the results.

15

Polyols

The following polyols are applicable to this invention: polyether polyols, polyester polyols, hydroxyl terminated polybutadiene and their copolymer with acrylonitrile, cinnoleic 20 triglyceride (commercially known as "castor oil"), and other vegetable oils of similar nature with different functionality and molecular weight.

A polyol which is particularly suited for use in the invention is polypropylene glycol, with the below specifications:

25	Hydroxyl number mg/KOH/gm	102-115
	Acid Number (Max.)	0.04 to 0.05
	Unsaturation (meq/g, max.)	0.025 to 0.028
	Functionality	2
30	Density lbs/gal @ 25°C	8.00-8.50
	Viscosity, CPS @ 25°C	75-80

The particular suppliers of this polyol include but are not limited to BASF Corporation, USA and Dow Chemical Company, USA.

Isocyanates

35 Isocyanates which can be utilized with this invention include diphenylmethane diisocyanates ("MDI"), toluene diisocyanates ("TDI"), hexamethylene diisocyanates ("HMDI"), and isophorone diisocyanates ("IPDI"). All of these have a functionality of two or greater.

An isocyanate which is particularly suited for use in this composition is MDI, with the below specifications:

5	Appearance	Dark brown liquid
	NCO content, wt %	32-35
	Viscosity @ 25°C, cps	70-75
	Flash point °C (COC)	>200°C
	Density @ 25°C, g/cm³	1.2-1.3

Suppliers of this isocyanate include but are not limited to BASF Corporation, USA and Dow Chemical Company, USA.

10 Figure 3 shows the results from a series of controlled experiments that show the impact of varying the amount of isocyanate. Formulation 1 is a preferred embodiment containing ten percent (10%) by weight isocyanate. Formulation 6 contains only nine percent (9%) by weight of isocyanate. By reducing the amount 15 of isocyanate, the gelation of the product can be controlled.

Catalyst

20 Catalysts applicable to this invention include dibutyltin dilaurate, dioctyltin dilaurate, different tertiary amines and organometallic compounds of tin, lead, cobalt, and zinc.

A catalyst which is particularly suited for use in this invention is dibutyltindilaurate ("Dabco T-12"), with the following specifications:

25	Flash point °C (PMCC)	>100°C
	Viscosity @ 25°C, cps	125
	Specific gravity at 25°C	1.05
	Water solubility	Soluble
	Appearance	Oily liquid
	Calculated OH Number, MgkOH/g	0

30 A supplier of this catalyst is Air Products and Chemicals, USA.

Figure 3 is a table of experimental results showing the effect of including a catalyst within the formulation. Formulation 1 is a preferred embodiment of the formulation and includes a trace amount of catalyst and four percent (4%) by weight of a curative agent. Formulation 1 produces an instantaneous induction time and a gelation time of fifty (50) seconds. Induction time is the time required for the viscosity of the formulation to begin increasing as a result of polymerization. Gelation time is the time required 35 for the viscosity effectively to reach infinity. Formulation 2 demonstrates the effect of not including the catalyst: the 40

induction time is sixty seconds and the viscosity of the formulation reaches a plateau after 210 seconds.

Curing agent

5 Curing agents applicable to this invention are those generally utilized with polyurethanes and specifically include the following: 3,5-dimethylthio-2,6-toluenediamine, 3,5-dimethylthio-2,4-tolunediamine, hexamethylene diamine, and trimethylol propane. In
10 addition, the invention includes those products sold under the following tradenames: ETHACURE-100 and ETHACURE-300 both available from Albermarle; and JEFFAMINE-400 available from Huntsman.

Figure 3 shows the results of a series of controlled experiments demonstrating the effect of curing agents. Formulation 1 shows a preferred embodiment of the invention. Formulation 3 a, b, and c show the effect of increasing the curing agent from zero to six percent (0 - 6%) by weight. The inclusion of greater amounts of curing agent reduced both the induction time and the gelation time. However, above four percent (4%) curing agent, full gelation is never reached. From this result, the conclusion that
20 the high concentrations of curing agent begin to interfere with the formation of high-molecular-weight polymers. Formulation 4 includes no catalyst and no curing agent. The result was a formulation having a delayed induction time and gelation time.

Figure 4 is a table showing the effect on gelation time that the different curing agents create. For purposes of forming a waterproofing membrane, a gelation time of sixty (60) seconds is preferred. For other applications, different gelation times may be more desirable.

30 Bituminous Material

Bituminous materials are a broad class of carbon-rich materials that typically have a high penetration index number ("PIN"). Examples of bituminous materials include the numerous grades of asphalt, performance grade asphalt (also known as polymer modified asphalt), and coal tar.

Asphalts can be described by their penetration index numbers. While all asphalts are included in this invention, experiments were

conducted on Type I, II, III, and IV asphalts having PINs ranging from 16 to 37.

5 Performance grade asphalts also can be described by their penetration index numbers. While all performance grade asphalts are included in this invention, experiments were conducted on the following types: 70/28, 64/28, 58/28, and 52/34 having PINs ranging from 65 to 195.

10 Hot mix asphalt is an asphalt that is heated up to certain temperatures so that certain additives can be incorporated into it, which creates a new composition. Preferably, the amount of rubberized asphalt in the invention is 40%-60% by weight.

15 Polymer modified asphalt is an asphalt that is modified with the integration of certain polymers, both virgin and recycled. Polymer modified asphalts improve the property, performance, and applications of asphalt.

Different kinds of polymers integrated into the asphalt may include polyethylenes, polypropylenes, polystyrenes, different block, graft, and random copolymers, virgin rubber, and rubber from crumb rubber.

20 Overall range of crumb rubber content in the asphalt is zero to seventy percent (0 - 70 %) by weight. The particular range (preferred range) used in this invention is between five and twenty-five percent (5 - 25%) by weight.

25 The polyol available for combinations in this invention are referenced above. The different combinations of polyols will be quantitatively premixed, in any combination, and calculated amounts of catalyst are mixed to optimize the various compositions in meeting the requirements of the particular application. The polyol used in one application of the invention is catalyzed polyol.

30 An example of the dibutyltindilaureate is sold under the trademark Dabco T-12 by Air Products and Chemicals, PA, USA. Details of Dabco T-12 are contained in the attached Polyurethane Additives Product Bulletin which is incorporated by reference herein as though fully set forth herein. The preferred range used in this composition is from 0.001 to 0.05 percent by weight.

35 The preferred isocyanate used in this composition is MDI, generally described above.

A suitable rubberized asphalt used for this composition contains crumb rubber from recycled car and truck tires of particle sizes ranging between ten and eighty (10 - 80) mesh. A supplier of this material is Bitumar, Inc., Canada.

5 Figure 3 depicts a series of controlled experiments that show the effect that the concentration of asphalt has on induction time and gelation time. As shown in Formulations 5a, 5b, and 1, as the concentration of asphalt increases the gelation time increases.
10 The data also shows that regardless of the asphalt concentration, the induction time remains instantaneous.

Figure 3 also shows the effect of temperature on the reaction. Formulation 5d was conducted at 100° F while formulation 5c was conducted at 250° F. At the higher temperature, the product containing no asphalt never fully gelled. In contrast at 100° F, 15 the formula gelled after only 15 seconds.

Figure 5 shows the results from a series of controlled experiments wherein the type of asphalt is changed to demonstrate its effect on gelation time. By changing the type of asphalt, the gelation time can be controlled for different applications.
20 Greater gelation times may be useful in applications such as adhesives. Partially gelled products can be used as elastomers for O-rings.

Application of Composition to Substrate

25 The procedure for application of the invention involves four steps: a) pumping; b) metering; c) polymerization; and d) spraying (collectively referred to as "Process"), shown schematically in Figure 1.

(a) Pumping step

30 The raw materials, isocyanate ("I"), polyol ("P"), catalyst ("C"), and rubberized asphalt ("RA") are pumped or supplied to the mixing apparatus 20. P and C are premixed at mixer 22 and supplied together as one component ("PC"). I and RA are supplied as the other two components. PC, I, and RA are supplied directly from their containers through heated hoses 24, 26 and 28 connected to feed pumps 25, 27 and 29, respectively in varying amounts or ratios as governed by controller 40.

(b) Metering step

The raw materials as received into the mixing apparatus are regulated by computerized controller 40, flow meters measuring 30, 32 and 34, and thermocouples 35, 37 and 39 measuring the temperatures.

5 (c) Polymerization step

The raw materials RA, I and PC are supplied to the mixing apparatus 20 where the *in situ* polymerization reaction is initiated by mixing the materials intensely so that a three-dimensional, semi-interpenetrating network molecular structure formation begins.

10 This reaction process continues while the mixture flows from the mixing chamber 20 to the conduit 50, where polymer propagation takes place without allowing complete cross-linking. The entire apparatus is preferably heated so as to accelerate the reaction rate and maintain the composition at the desired temperature. The 15 resulting prepolymer is conveyed from the reaction chamber to the spraying device 80.

The preferred amount of polyurethane prepolymer in the invention is between thirty and fifty (30% - 50%) by weight. It should be noted that the entire apparatus shown in Fig. 1 is 20 preferably heated, including all supply lines and mixing chambers, so that the ingredients and resulting composition are maintained at a temperature in the range of 300°F - 340°F.

The preferred ratio of polyol/isocyanate to rubberized asphalt is 50:50. The preferred ratio of polyol to isocyanate is 80:20. 25 The catalyst is 0.07% by weight of the polyol composition.

(d) Spraying step

The prepolymer 70 travels to the spraying device 80, where it is sprayed out of a nozzle and onto the surface or substrate S to be coated.

30

Varying the Compositions

Depending upon the application, required amounts of all of the raw materials will be processed through the above-described process and applied to the different substrates. The properties of the 35 composition, nature of the substrates, application conditions, and other related factors determine the resulting coating.

The prepolymers created by this invention will have reactive isocyanate terminal groups and will cure with moisture and/or any

molecules with active hydrogen atoms. The overall range of the polyurethane prepolymers is between ten and ninety percent (10% - 90%) by weight.

The instant invention that has been shown and described herein is considered to be the most practical and preferred embodiment. It is recognized, however, that departures may be made therefrom within the scope of the invention and that obvious modifications will occur to a person skilled in the art.

10

INDUSTRIAL APPLICABILITY

The industrial applicability can be understood by analyzing the objects of the invention and the problems that are solved by accomplishing these objects.

An object of the present invention is to provide a composition which is superior in providing coating and sealing over a substrate.

Another object of this invention is to provide a method of preparing such a composition at or near the site of application, easily and economically.

Another object of this invention is to provide a sealing and coating composition which provides superior traction performance.

CLAIMS

The claims are as follows:

1. A bituminous polyurethane interpenetrating elastomeric composition comprising:

5 a bituminous material,
 a polyol, and
 an isocyanate.

10 2. The composition as described in claim 1 wherein said bituminous material is between zero and seventy-five percent by weight of said composition.

15 3. The composition as described in claim 1 wherein said bituminous material has a penetration index number between 16 and 195.

4. The composition as described in claim 1, wherein said bituminous material is a coal tar.

20 5. The composition as described in claim 1, wherein said bituminous material is a performance graded asphalt.

25 6. The composition as described in claim 1, wherein said bituminous material is a rubberized asphalt containing a polymer chosen from the group consisting of polyethylene, polypropylene, polystyrene, virgin rubber, and crumb rubber.

30 7. The composition as described in claim 6, wherein said polymer comprises between zero and seventy percent by weight of said bituminous material.

8. The composition as described in claim 1, wherein said polyol is between thirty-four and seventy-two percent by weight of said composition.

35 9. The composition as described in claim 1, wherein said polyol is chosen from the groups consisting of polypropylene glycol, polyether polyol, polyester polyol, hydroxyl terminated

polybutadiene, copolymer containing acrylonitrile, cincinoleic triglyceride, and vegetable oil.

10. The composition as described in claim 1, wherein said
5 isocyanate is between five and twenty percent by weight of said
composition.

11. The composition as described in claim 1, wherein said
isocyanate is chosen from the group consisting of diphenylmethane
10 diisocyanate, toluene diisocyanate, hexamethylene diisocyanate, and
isophorone diisocyanate.

12. The composition as described in claim 1, further comprising
a curing agent.

15 13. The composition as described in claim 12, wherein said curing
agent is between zero and eight percent by weight of said
composition.

20 14. The composition as described in claim 12, wherein said curing
agent is chosen from the group consisting of Ethacure-100,
Ethacure-300, Jeffamine-400, hexamethylene diamine, trimethylol
propane, 3,5-dimethylthio-2,6-toluenediamine, 3,5-dimethylthio-2,4-
toluenediamine, and similar di and poly functional amines.

25 15. The composition as described in claim 1, further comprising
a catalyst.

30 16. The composition as described in claim 15, wherein the amount
of said catalyst is trace.

17. The composition as described in claim 15, wherein the amount
of catalyst is between one and five percent by weight of said
polyol.

35 18. The composition as described in claim 15, wherein said
catalyst is chosen from the group consisting of dibutyltin
dilaurate, dioctyltin dilaurate, tertiary amine, and organometallic

compounds of tin, organometallic compounds of lead, organometallic compounds of cobalt, and organometallic compounds of zinc.

19. A bituminous polyurethane interpenetrating elastomeric network
5 composition comprising:

fifty percent by weight of rubberized asphalt having a penetration index number of 30,

thirty-six percent by weight of polyether polyol,

10 four percent by weight of 3,5-dimethylthio-2,6-toluenediamine and 3,5-dimethylthio-2,4-toluenediamine,

a trace amount of dibutyltin dilaurate, and

ten percent by weight of polymeric MDI.

20. A method of preparing a bituminous polyurethane interpenetrating elastomeric network composition comprising a bituminous material, a polyol, and an isocyanate; said method comprising:

15 heating said bituminous material in a first container at least to its molten temperature,

mixing said polyol in a second container,

mixing said bituminous material and said polyol together to form a reagent mixture, and

25 adding said isocyanate to said reagent mixture to form said bituminous polyurethane interpenetrating elastomeric network composition.

21. The method described in claim 20 further comprising adding a catalyst to said second container before mixing with said bituminous material.

30 22. The method described in claim 20 further comprising adding a curing agent to said second container before mixing with said bituminous material.

35 23. The method described in claim 20 further comprising spraying said bituminous polyurethane interpenetrating elastomeric network composition onto a substrate after mixing said isocyanate with said reagent mixture.

24. The method as described in claim 20 further comprising:
adjusting the composition to adjust the gelation time.

5 25. The method as described in claim 20 further comprising:
adjusting the composition to adjust the induction time.

26. The method described in claim 20 wherein said bituminous material is heated to a temperature between 125°C and 225°C.

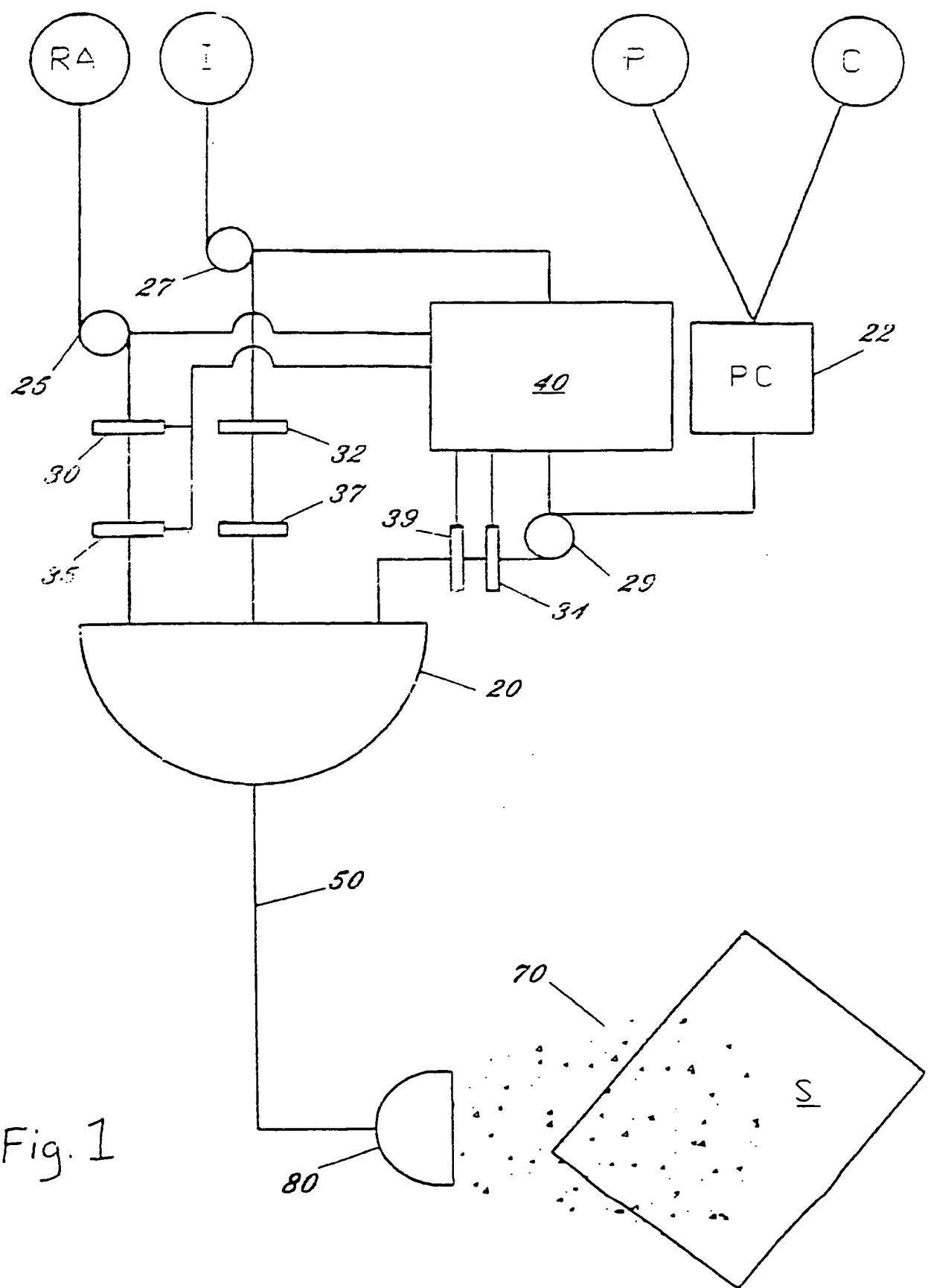
10 27. A bituminous polyurethane interpenetrating elastomeric network composition comprising a bituminous material, a polyol, and an isocyanate; said composition made through the method comprising:
heating said bituminous material in a first container at least to its molten temperature,

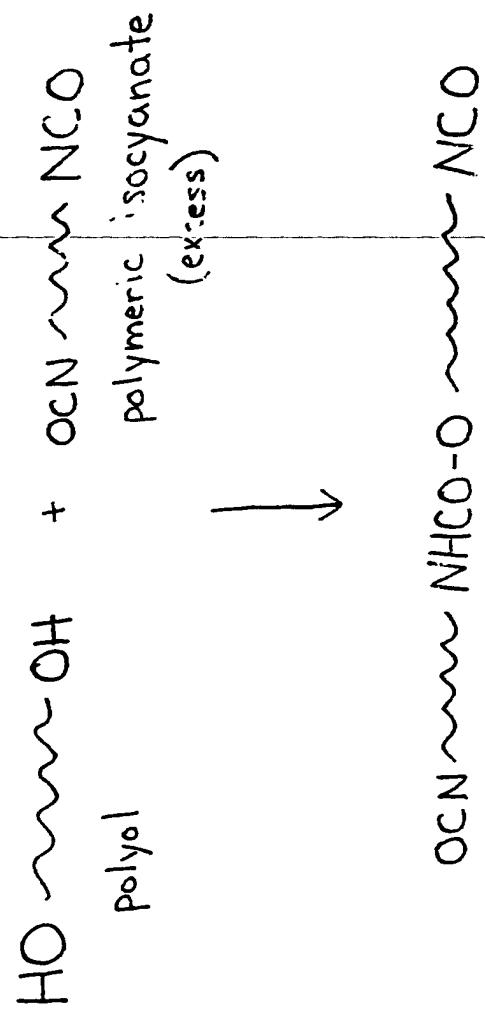
15 mixing said polyol in a second container,

mixing said bituminous material and said polyol together to form a reagent mixture, and

adding said isocyanate to said reagent mixture to form said bituminous polyurethane interpenetrating elastomeric network

20 composition.





Prior Art Fig. 2

Gelation kinetics of Asphalt-Polyurethane IPN formation.

<i>Variation of components</i>	<i>Asphalt</i>	<i>Poly Curative</i>	<i>Catalyst</i>	<i>Iso</i>	<i>Induction Time</i>	<i>Gelation Time</i>
1. Preferred Embedment	50%	36%	4%	Trace	10%	Instantaneous
2. Effect of Catalyst	50%	36%	4%	Nil	10%	60 sec.
3. a) Absence of Curative	50%	40%	Nil	Trace	10%	180 sec.
b) Role of Curative %	50%	34%	6%	Trace	10%	partial gelation
c) Role of Curative %	50%	38%	2%	Trace	10%	165 sec.
4. Absence of Curative and Catalyst	50%	40%	Nil	Nil	10%	420 sec.
5. a) Effect of asphalt	25%	36%	4%	Trace	10%	Instantaneous
b) Effect of asphalt	75%	36%	4%	Trace	10%	375 sec, partial gelation
c) Effect of asphalt	Nil	72%	8%	Trace	20%	60 sec, partial gelation
d) Effect of asphalt*	Nil	72%	8%	Trace	20%	Instantaneous
6. Variation of Iso %	50%	37%	4%	Trace	9%	40 sec, partial gelation

Temperature: $250 \pm 3^\circ\text{C}$
 Stirring 200 RPM
 Percentage of composition (%) by weight.
 * Temperature = $100 \pm 3^\circ\text{C}$

Fig. 3

FIGURE 4
GELATION REACTION KINETICS USING DIFFERENT CURING AGENTS

SUPPLIER	CURING AGENT TRADENAME	CURING AGENT GENERIC NAME AND CAS NO.	GELATION TIME (sec)
Albermarle	Ethacure-100	Diethyltoluenediamine 68479-98-1	instantaneous
Albermarle	Ethacure-300	Di-(methylthio)toluenediamine 106264-79-3	60
Huntsman	Jeffamine-400	Poly(oxy(methyl-1,2,-ethanediyl),alpha-hydro- Omega-(2-aminomethyl)ethylhexyl)-ether with 2-ethyl- 2-(hydroxymethyl)-1,3-propanediol (3:1) 39423-51-3	100
DuPont	Hexamethylene diamine	Hexamethylenediamine (1,6-Hexanediamine)	10
Dupont	Trimethylol Propane	Trimethylolpropane 77-99-6	incomplete gelation

FIGURE 5

GELATION REACTION KINETCS USING DIFFERENT BITUMINOUS MATERIALS

BITUMINOUS MATERIAL	GELATION TIME (sec)
Built up Roof Grade Asphalt	
Type I (PIN 37 at 25°C)	40
Type II (PIN 23 at 25°C)	60
Type III (PIN 18 at 25°C)	20
Type IV (PIN 16 at 25°C)	45
Coal Tar	35
Performance Grade Asphalt	
PG 70/28 (PIN 65 at 25°C)	60
PG 64/28 (PIN 75 at 25°C)	50
PG 58/28 (PIN 105 at 25°C)	105
PG 52/34 (PIN 195 at 25°C)	semi gelation

Experiments were run at 250° F, and mixed at 200 RPM.
asphalts supplied by Bitumar, Inc.

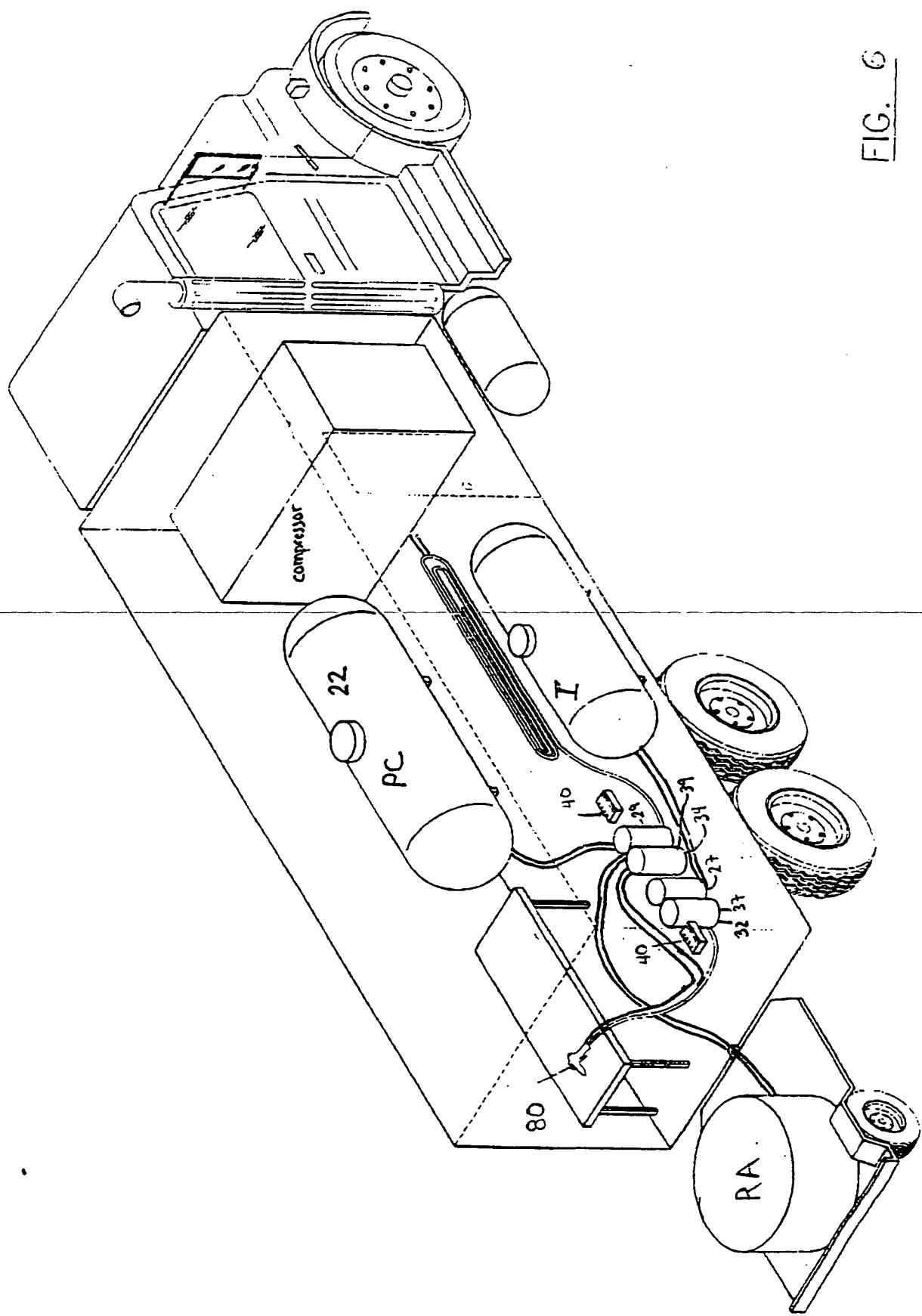
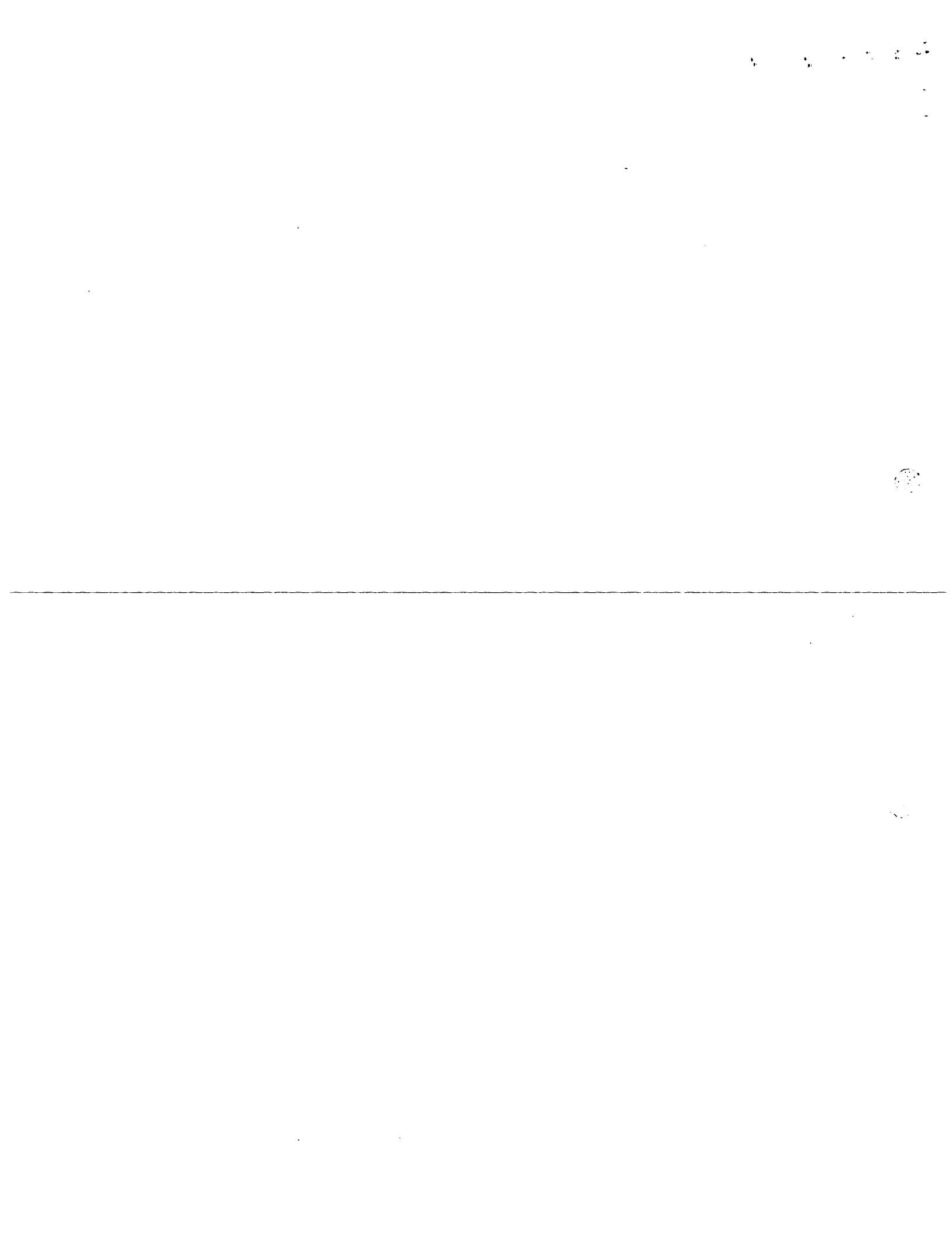


FIGURE 7

MOST PREFERRED METHODS AND MATERIALS

MATERIALS	SPECIFICATIONS	SUPPLIERS
Rubberized Asphalt	30 PIN	Bitumar Inc., Montreal Canada
Polyether Polyol	MW = 1000 d @ 25°C=0.97 g/cm ³ Functionality=2.00	BASF Corporation, Mount Olive, New Jersey, USA
Polymeric MDI	Functionality=1.2 d @25°C=1.22 NCO Content=32%wt (CAS No.9016-87-9)	BASF Corporation, Mount Olive, New Jersey, USA
Curing Agent	Mixture of 3,5-dimethylthio-2,6-toluenediamine & 3,5-dimethylthio-2,4-toluenediamine (CAS No. 106264-79-3)	Albermarle Corporation, Louisiana, USA
Catalyst	Dibutyltin dilaurate (CAS No. 77-58-7)	Air Products and Chemicals, Allentown, PA





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<p>(54) Title: BITUMINOUS POLYURETHANE INTERPENETRATING ELASTOMERIC NETWORK COMPOSITIONS</p> <p>(57) Abstract</p> <p>The elastomeric polyurethane interpenetrating network compositions of the invention are developed by in situ reaction of polyols with different isocyanates and polyisocyanates in bituminous material. (2) Suitable bituminous materials include asphalt, coal tar, polymer modified asphalt, oxidized, and unoxidized asphalt. (3) The composition is preferably formed at a temperature between 200 ° F and 350 ° F. The reaction kinetics can be accelerated by including catalysts and curing agents. (4) The bituminous polyurethane interpenetrating network elastomeric compositions were hot-sprayed-applied (200 ° F-350 ° F) on concrete, metal, wood, built-up roofing systems, polyurethane foams, and other construction materials with a specially designed spray applicator system. (1) The coated substrates were evaluated for their physical and mechanical properties, adhesion, static and dynamic puncture resistance, wind-up lift test, and other properties. Bituminous polyurethane interpenetrating network elastomers are suitable for roofing, new construction, and wall and foundation waterproofing applications (7).</p>			

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/18929

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US CL :427/138, 421, 422; 524/59, 705

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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U.S. : 427/138, 421, 422; 524/59, 705

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3,637,558 A (VERDOL et al.) 25 January, 1972. See entire document.	1-13, 15-18, 24-27, 20-22
X	US, 4,195,009 A (ZIMMERMANN) 25 March, 1980. See Abstract and Examples 1-4.	1-13, 15-18, 24-27, 20-22
X	US 4,443,578 A (FRIER) 17 April, 1984. See claims 1-3 and column 2, lines 44-48.	1-13, 15-18, 24-27, 20-22
X	BE 753,865 A (NAPHTACHIMIE SA) 25 January, 1971. See Abstract.	1-13, 15-18, 24-27, 20-22
X	JP 47-13981 A (TAKEDA CHEMICAL INDs LTD) 26 April, 1972. See Abstract.	1-13, 15-18, 24-27, 20-22

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X	BP 1,323,884 A (IMPERIAL CHEMICAL INDUSTRIES) 18 July, 1973. See claim 11 and Examples.	1-13, 15-18, 24-27 20-22
X	JP 10337 A (NITTETSU CHEM) 25 January, 1980. See Abstract.	1-13, 15-18, 24-27
X	JP 61-126125 A (IDEMITSU PETROCHEM KK) 13 June, 1986. See Abstract.	1-13, 15-18, 24-27, 20-22
X	JP 61-174282 A (IDEMITSU PETROCHEM KK) 05 August, 1986. See Abstract.	1-13, 15-18, 24-27, 20-22
X	JP 62-53371 A (NICHIREKI KAGAKU KO) 09 March, 1987. See Abstract.	1-13, 15-18, 20-22, 24-27
X	EP 0,219,399 A (SCREG ROUTES & TRAV) 22 APRIL 1987. See Abstract.	1-13, 15-18, 20-22, 24- 27
Y	US 3,645,945 A (LESESNE et al.) 29 February, 1972. See entire document.	1-27
Y	US 3,835,077 A (MORI et al.) 10 September 1974 See Example 1.	1-27
Y	US 3,880,789 A (ISHIHARA et al.) 29 April, 1975. See claim 1.	1-27
Y	US 5,077,349 A (FEHLBIER et al.) 31 December, 1991. See claims 1, 3 and 10.	1-27
Y	US, 5,045,590 A (MOTOMURA et al.) 03 September, 1991. See entire document.	1-27
Y	US 5,714,563 A (DEPOMPEI et al.) 03 February 1998. See Table I.	1-27
Y	DE 2,554,864 A1 (LION OIL CO) 16 June, 1976. See Abstract.	1-27
Y	JP 56-98259 A (DAIICHI KOGYO SEIYAKU) 07 August, 1981. See Abstract.	1-27
Y	SU 0587725 A(SMIRNOV B P) 30 January 1980. See Abstract.	1-13,15-18, 24-27, 20-22
Y	US 3,179,610 A (WOOD) 20 April 1965. See claim 1.	1-27

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